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Laser Raman and FTIR spectra of 2,3,5-Tri-iodobenzoic acid

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Abstract The Stokes as well as anti- Stokes Laser Raman spectra of 2,3,5-tri-iodobenzoic acid have been recorded in the regions 150-4000 cm^{-1} on Spectra Pro-500 Laser Raman Spectrometer using 4880 A^{0} emission line of Argon ion Laser as a source of excitation FTIR spectra of above compound have also been recorded in solid phase as well as in liquid phase in the regions 400-4000 cm^{-1} on Perkin Elmer FTIR spectrophotometer The normal analysis has been carried out by taking this molecule to belong to Cs- point group The observed frequencies were assigned to various modes of vibration on the basis of intensity, frequencies from similar molecules.

Keywords Laser Raman spectra, FTIR spectra, 2,3,5-tri-iodobenzoic acid

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Introduction

substituted benzene derivatives has been the subject of roscopic investigation in infrared region. The FTIR and Raman spectra of benzoic acid and mono-substituted ic acid have been studied by several workers [1-5]. Fletts 1955, has reported vibrational spectra of sixty corboxlic Green [2] in 1977, has reported the complete analysis of ic acid and some substituted benzoic acids. Ansari and a[3] have reported spectral studied of benzoic acid, Phthalic and salicylic acid. Rastogi *et al* [4] have reported the tional study of 3,5-di-nitro benzoic acid. Mohan and Arul [5] have reported the vibrational study of para-obenzoic acid. However, there is no report on vibrational ra of 2,3,5-tri-iodobenzoic acid in the literature. Therefore, desirable to record the FTIR and Laser Raman spectra of -tri-iodobenzoic acid and to study the complete vibrational ysis on the basis of Cs-point group.

Experimental details

chemical 2,3,5-tri-iodobenzoic acid is a white crystalline It was obtained from SpectroChem. Pvt. Ltd., Mumbai and used as such. FTIR spectrum of above compound was recorded in the region 400-4000 cm^{-1} in solid phase as well as in liquid phase on Perkin-Elmer FTIR spectrophotometer in the Chemistry department of Delhi University, Delhi. The Stokes as well as anti-Stokes Laser Raman spectra of above compound have been recorded on Spectra-Pro-500 Laser Raman spectrophotometer using 4880 Å radiation from an Argon ion Laser operating at 4W. These were recorded in M. N. Saha Spectroscopy Laboratory of Allahabad University's Physics Department, Allahabad. These spectra have been shown in the Figures 1-4.

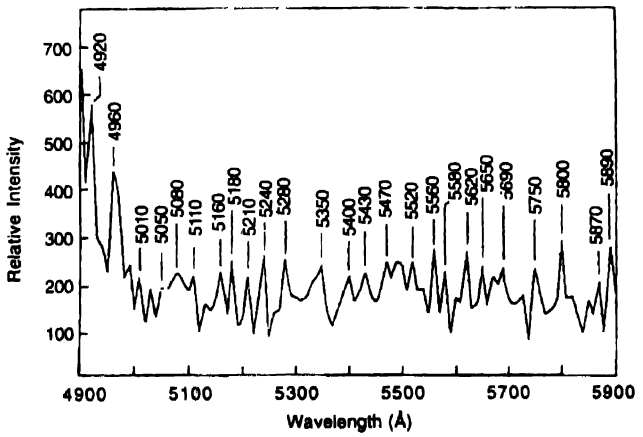

Figure 1. Stoke's Laser Raman spectrum of 2, 3, 5-tri-iodobenzoic acid.

ponding Author

In these spectra, the positions of Stokes and anti- Stokes lines have been shown in wavelengths (Å). In order to get the frequencies of Stokes lines and anti-Stokes lines, the following procedure has been used. The wavelengths of these positions have been converted into the corresponding wave numbers and these wave numbers have been subtracted from the wave number corresponding to the exciting line. Therefore in the Table 1, the frequencies of Stokes as well as the frequencies of anti-Stokes lines have been shown in cm^{-1}.

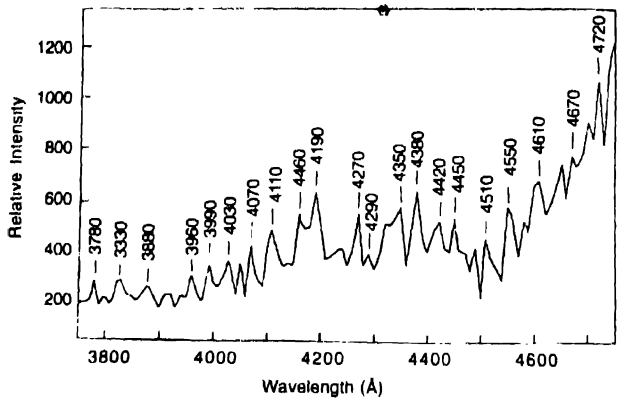

Figure 2. Anti-Stoke's Laser Raman spectrum of 2, 3, 5-tri-iodobenzoic acid

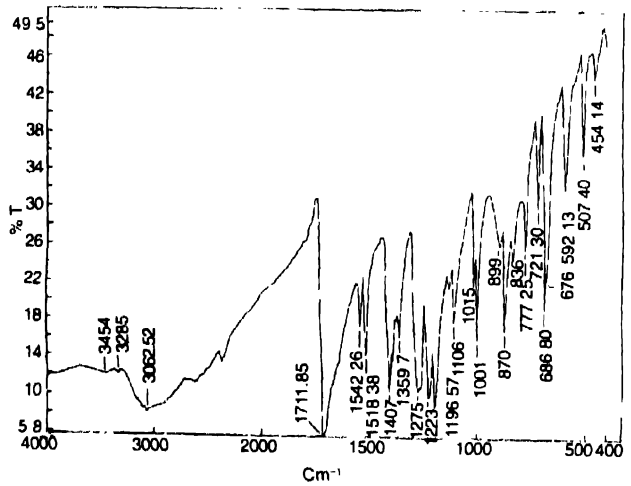

Figure 3. FTIR spectrum of 2, 3, 5-tri-iodobenzoic acid

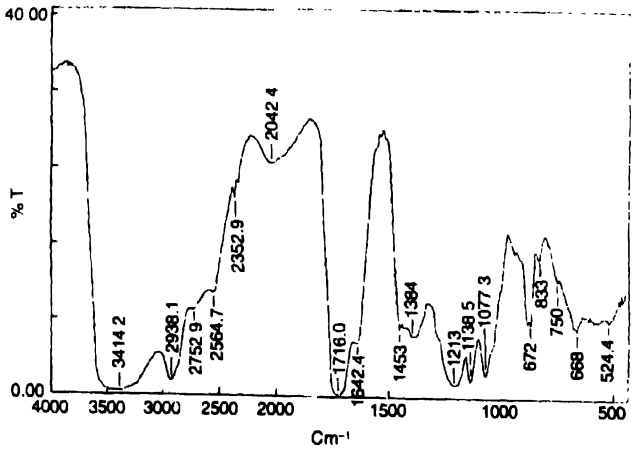

Figure 4. FTIR spectrum of 2, 3, 5-tri-iodobenzoic acid in 1, 4-dioxane.

Table 1 Observed vibrational frequencies in FTIR and Laser Raman spectrum of 2 3,5-tri-iodobenzoic acid.

FTIR (cm^{-1})	L.R. (cm^{-1}) Stoke's	anti-stoke's	Symmetry species	Assignments
	166		a"	C-I o p b
	330		a'	C-I i p b
454	451		a'	C-I stretch
507	531		a'	C-I stretch
592	610		a'	C-I stretch
676			a"	C-C o p b
686	689	694	a"	C-C o p b
721			a"	C-C o p b
777		784	a"	C-C o p b
	806		a"	C-H o p b
836			a"	C-H o p b
870			a"	C-H o p b
899	922	921	a"	C-OH o p b
1001	998		a'	C C ring breathing vib.
1015		1013	a'	C-C i p b
1106	1111		a'	C-C i p b
1196	1186	1199	a'	C-C i p b
1223			a'	C-O stretch
1275	1297		a'	C-H i p b
1359		1341	a'	C-H i p b
1375		1152	a'	C-OH i p b
1397			a'	C-C stretch
1407	1407		a'	C-C stretch
		1485	a'	C-C stretch
1518			a'	C-C stretch
1542	1551		a'	C-C stretch
1568			a'	C-C stretch
1711		1680	a'	C=O stretch
1785	1799	1779	A"	(1001+777)
1807			A'	(1223+592)
1955	1972	1979	A'	(1359+592)
	2074		A'	(1551+531)
2114			A'	(1106+1015)
		2132	A"	(1199+921)
	2209		A"	(1297+922)
2341		2338	A"	(1568+777)
2360			A'	(1359+1001)
	2375		A'	(2x 1186)
	2505	2495	A'	(1407+1111)
2546			A'	(1542+1001)
	2569			

Contd

FTIR (cm^{-1})	L.R (cm^{-1}) Stoke's	anti-stoke's	Symmetry species	Assignments
2637	2633		A'	(1359+1275)
	2697			
2705			A'	(1711+1001)
	2791			
		2817	A'	(1485+1341)
	2854		A'	(1551+1297)
2932	2916	2926	A'	(1518+407)
3022	3038		a'	C-H stretch
3062	3099		a'	C-H stretch
3122			A'	(1711+1407)
	3249			
3285			A'	(1711+1568)
	3316			
3454	3396	3373	a'	O-H stretch

i p b = in-plane-bending, o p b = out-of-plane bending, stretch= stretching

Table 2 Observed frequency shift in 2,3,5 – tri-iodobenzoic acid in 1,4 Dioxane

FTIR frequencies (cm^{-1})	FRTIR frequencies in solvent (cm^{-1})	Frequency shift (cm^{-1})	Mode
3454	3414.2	39 8	O-H stretching
1711	1716 0	5.0	C=O stretching
1568	1559.0	7.0	C- C stretching
1542	1536.2	6 2	C–C stretching
1518	1512 1	6 1	C–C stretching
1407	1428	21.0	C–C stretching
1397	1384.2	9 2	C–C stretching
1223	1213 6	10 6	C–O stretching
1196	1138	58 0	C–C i.p.b.
1015	1077 3	62 3	C–C i p.b.
899	881.4	18 4	C–OH def o.o.p
886	833	3.0	C–H o.p.b
721	750	29 0	C–C o p.b
676	668	8.0	C–C o p b
507	524.4	17.4	C–I stretching

i p b – in-plane bending, def. o.o.p. – deformation out of plane bending, o p b – out of plane bending

3. Discussions and analysis

The molecule 2,3,5-tri-iodobenzoic acid is a tri-substituted benzoic acid or we can say that it is a tetra-substituted benzene. The vibrational bands observed in the infrared region are very sharp, broad and less intense. All these bands have been assigned in terms of various fundamentals combination vibrations. This molecule belongs to Cs-point group. In this point group, there are two types of vibrations, planar (a') and non-planar (a") occur. The observed fundamental frequencies and their probable assignments are presented in the Table 1. Table 2 describes the observed frequency shifts due to solvent effect. Since the vibrational spectrum of a molecule is affected by environmental factors, as a result the changes in the shape, frequency and intensity of the bands are observed. The shift in O-H stretching vibration may be due to hydrogen bonding with 2,3,5- tri-iodobenzoic acid. Shift in C=O stretching vibration is due to the strong interaction of the parent molecule with the 1,4 dioxane. In other vibrations as well as the molecular interaction with the parent compound is more pronounced. Solvent shift is obtained in most of the stretching vibrations and out-of-plane vibrations. C-I stretching vibration of 507 cm^{-1} has been increased to 524 cm^{-1}. This shift in the C-I stretching vibration is due to heavy mass of Iodine atom being influenced by 1,4 dioxane solvent.

3.1. C-H Vibrations :

In aromatic compounds, C-H stretching frequencies appear in the range of 3000-3100 cm^{-1}, C-H in plane bending in the range of 1000-1300 cm^{-1} and C-H out of plane bending vibration in the range 750-1000 cm^{-1}. There are six C-H stretching frequencies in the benzene with following modes of the vibration a_{1g}(3062 cm^{-1}), b_{1u}(3060 cm^{-1}), c_{2g}(3047 cm^{-1}) and c_{1u} (3099 cm-1). Last two modes are doubly degenerated. In the present case, the frequencies 3060 cm^{-1} and 3022 cm^{-1} are assigned for C-H stretching modes in the 2,3,5-tri-iodobenzoic acid in FTIR spectrum of compound. These bands are observed at 3038 cm^{-1} and 3099 cm^{-1} in the Laser Raman spectrum. These assignments are in good agreement with [6,7]. The six C-H in plane bending vibrations are derived from a_{2g}(1340 cm^{-1}), b_{2u}(1037 cm^{-1}), c_{2g}(1178 cm^{-1}), e_{1u}(1037cm^{-1}) modes of benzene . The frequencies 1359 cm^{-1} and 1275 $cm^{-1}$are assigned for C-H in plane bending and are in favorable agreement with values given in the literatures [8, 9]. The out of plane bending vibrations in the benzene arise from b_{2g}(995 cm^{-1}), e_{2u}(975 cm^{-1}), e_{1g}(849 cm^{-1}) and a_{2u} (671 cm^{-1}) modes of benzene. The frequencies 836 cm^{-1} and 870 cm^{-1} have been assigned to C-H out of plane bending vibrations. These assignments are in agreement with those of previous workers[10-12]. In this molecule, we have observed only two C-H stretching, two C-H in plane and two out of plane bending vibrations due to the fact that four other vibrations will correspond to the substituents.

3.2. C-C Vibrations :

Amongst the C-C ring stretching frequency of benzene, the ring breathing vibration a_{1g}(991 cm^{-1}) undergoes some change in its magnitude whereas other frequencies are affected slightly upon the substitution. The magnitude of the ring breathing vibration remains near about 1000 cm^{-1}. In the present case, a frequency observed at 1001 cm^{-1} has been assigned as ring breathing vibration. The four characteristics stretching modes of C-C in the benzene are, namely e_{2g} (1585 cm^{-1}), e_{1u}(1485 cm^{-1}), b_{2u}(1370 cm^{-1}) and a_{1g} (991 cm^{-1}). The frequencies 1010 cm^{-1}, 1568 cm^{-1},

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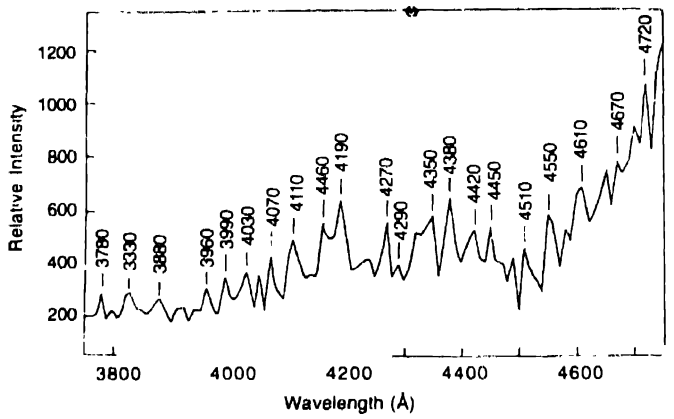
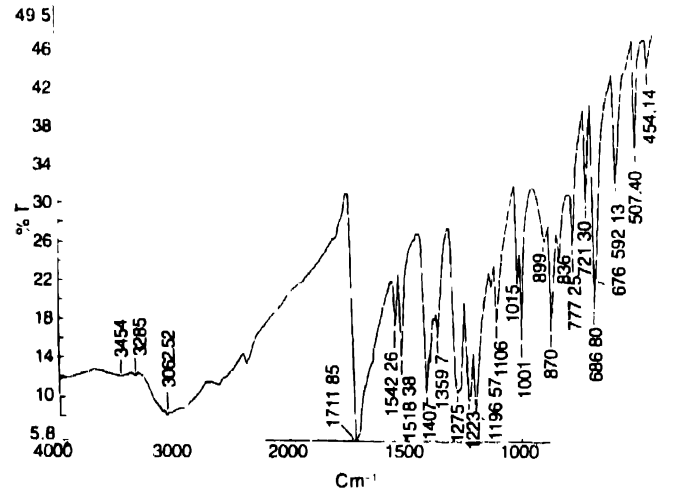


Figure 2. Anti-Stoke's Laser Raman spectrum of 2, 3, 5-tri-iodobenzoic acid



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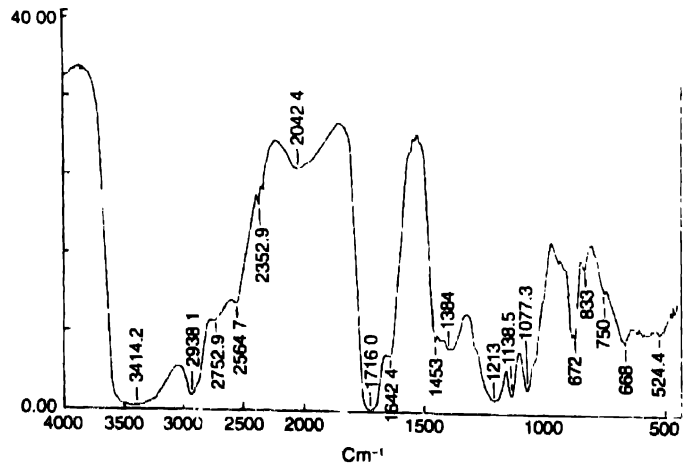

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1397			a'	C-C stretch
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1518			a'	C-C stretch
1542	1551	-	a'	C-C stretch
1568			a'	C-C stretch
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1542 cm^{-1}, 1518 cm^{-1}, 1407 cm^{-1} and 1397 cm^{-1} have been assigned as C-C stretching vibrations for the present molecule. The ring deformation frequencies in substituted benzenes are derived from e_{2g}(606 cm^{-1}),b_{2g}(703 cm^{-1}) and e_{2u}(405 cm^{-1}) modes of benzene. Modes e_{2g} (606 cm^{-1}) and e_{2u} (405 cm^{-1}) are doubly degenerate while mode b_{2g}(703 cm^{-1}) is non-degenerate . The frequencies at 1196 cm^{-1}, 1106 cm^{-1} and 1015 cm^{-1} have been assigned as C-C deformation in plane and frequencies at 771 cm^{-1}, 721 cm^{-1}, 686 cm^{-1} and 667 cm^{-1} have been assigned as C-C deformation out of plane for the present molecule.

3.3 COOH group vibrations .

O-H stretching band is characterized by very broad band appearing near about 3400 cm^{-1} The band observed at 3454 cm^{-1} has its origin in the O-H stretching vibration .The C = O stretching is a characteristic frequency of carboxylic acid. The band appearing at 1711cm^{-1} is assigned as C = O stretching vibration in FTIR spectrum and in the anti-Stokes Laser Raman spectrum this band has been assigned at 1680 cm^{-1} O-H bending in plane occurs between 1440-1395 cm^{-1} and out of plane bending occurs between 960-875 cm^{-1}. The frequency at 1375 cm^{-1} is assigned as OH in plane bending vibration and frequency at 899 cm^{-1} is assigned as OH out of plane bending vibration for the present molecule. The present assignments agree well with the values available in the literatures [13-17].

3.4. C-I Vibrations :

C-I stretching vibration appears near 500 cm^{-1} In the present investigation, the bands appearing at 454 cm^{-1}, 507 cm^{-1} and 592 cm^{-1} have been assigned to C-I stretching vibrations in FTIR spectrum of the compound The frequencies at 451 cm^{-1} and 531 cm^{-1} have been assigned to C-I stretching vibrations in Stokes Laser Raman spectrum of present molecule. The vibration has been assigned by Ahmed *et al* [18] at 454cm^{-1} in the p-iodo nitrobenzene. The bands observed at 166 cm^{-1} and 330 cm^{-1} have been assigned to C-I out of plane bending vibration and C-I in plane bending vibration in the Stokes Laser Raman spectrum respectively.

Acknowledgment

We are grateful to Chairman, Physics Department, Aligarh Muslim University, Aligarh for the encouragement and giving full financial assistance. We are thankful to the Head, Department of Chemistry, Delhi University, Delhi for providing facilities to record the FTIR spectrum of the compound. We are also thankful to the Head of M.N. Saha Spectroscopy Laboratory, Department of Physics, Allahabad University, Allahabad for recording Laser Raman spectrum of the compound.

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